Phase transitions, optical, dielectric and viscoelastic properties of colloidal suspensions of BaTiO$_3$ nanoparticles and cyanobiphenyl liquid crystals

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Phase transitions, optical, dielectric and viscoelastic properties of colloidal suspensions of BaTiO$_3$ nanoparticles and cyanobiphenyl liquid crystals

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We report experimental studies on the phase transitions and physical properties of colloidal suspensions of BaTiO$_3$ nanoparticles and two cyanobiphenyl liquid crystals (4-pentyl-4′-cyanobiphenyl and 4-octyl-4′-cyanobiphenyl). From the differential scanning calorimetric measurements, we show that the nanoparticles have antagonistic effect on the isotropic to nematic and nematic to smectic-A phase transitions. The birefringence, dielectric anisotropy and splay elastic constant remain almost unchanged, whereas the bend elastic constant and rotational viscosity decrease considerably. The experimental results are discussed based on the possible contribution of BaTiO$_3$ nanoparticles and free surfactant molecules in the suspensions.

Keywords: nanoparticles; liquid crystals; phase transitions; viscoelastic properties

1. Introduction

The study on the colloidal suspension of nanoparticles in liquid crystals is interesting from both the fundamental and technological points of view. The effect of dispersion of nanoparticles on various physical properties depend on an important length scale, called the extrapolation length ($\xi$), defined as the ratio between the typical elastic constant $K$ and the surface anchoring energy $W$. When the size of the nanoparticle, $R$, is much smaller than $\xi$, the molecules are not strongly pinned at the nanoparticles and there is no long-range elastic distortion. If the initial liquid crystal orientation is monodomain, it is likely to remain as such with no apparent evidence of dissolved nanoparticles. Although the molecular orientation does not change much, the small particles affect significantly the anisotropic physical properties that depends on the size, shape, concentration and properties of the nanoparticles.[1–6] There are several reports on the various physical measurements on liquid crystal nanocomposites based on ferromagnetic, ferroelectric, metal and inorganic nanoparticles.[7–15] The colloidal dispersion of these nanoparticles in liquid crystals combines the physical properties of nanoparticles and orientational order of liquid crystals. It has been reported that the several liquid crystal nanocomposites are useful for display applications.[16–21]

In this article, we present experimental results on the phase transitions and physical properties of colloidal suspension of two liquid crystals, namely, 4-pentyl-4′-cyanobiphenyl (5CB)- and 4-octyl-4′-cyanobiphenyl (8CB)-doped BaTiO$_3$ nanoparticles. We show from the thermal measurements that the nematic (N) temperature range of both the compounds have decreased while the smectic-A (SmA) temperature range is increased in 8CB. We measured birefringence, dielectric, curvature elastic constants and rotational viscosity at various temperatures by using an electrooptic technique. We show that birefringence, dielectric anisotropy and splay elastic constant are unchanged, whereas the bend elastic constant and rotational viscosity decrease.

2. Experimental

Indium-tin-oxide-coated (ITO) glass plates with circularly patterned electrode were used to make experimental cells. The ITO plates were spin-coated with polyimide AL-1254 and cured at 180°C for 1 h and rubbed antiparallel way for homogeneous alignment of the director (the average alignment direction of the molecules). For homeotropic alignment, plates were coated with JALS-204 and cured at 200°C for 1 h. Empty cells of different gaps in the range 5–13 µm were fabricated using appropriate spacers. Using an impedance analyser (Novocontrol, Alpha-A), the perpendicular and parallel components of the dielectric constant were measured in a planar and homeotropic cells, respectively. All the measurements were performed at a frequency 1 KHz by applying a very small voltage (much less than the Freedericksz’s threshold voltage) across the cell.

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Birefringence and elastic constants were measured using an electrooptic technique. The sample retardation was measured by using a helium-neon laser ($\lambda = 632.8$ nm), photoelastic modulator (PEM) and a lock-in amplifier.\[22, 23\] Using an LCR meter (Inductance-Capacitance-Resistance), sinusoidal voltage of frequency $1$ KHz and amplitude up to $20$ V was applied. The phase retardation and sample capacitance were measured simultaneously as a function of temperature and voltage. A photodetector collected the light transmitted through the liquid crystal, and lock-in amplifier measured the first and second harmonics of the ac signal. The first and second harmonics signals (1f and 2f signals) measured by the lock-in amplifier are given by $I_{1f} = I_0 J_1(A_0) \sin(\Delta \phi)$ and $I_{2f} = I_0 J_2(A_0) \cos(\Delta \phi)$ where $J_1(A_0)$ and $J_2(A_0)$ are first- and second-order Bessel coefficients, $I_0$ is the transmitted intensity and $\Delta \phi$ is the optical phase shift and $A_0 = 2.405$ is the retardation amplitude of the PEM. The birefringence of the sample is given by \[24\]

$$\Delta n = \frac{\lambda}{2 \pi d} \Delta \phi = \frac{\lambda}{2 \pi d} \arctan \left( \frac{I_{1f} \times J_2(A_0)}{I_{2f} \times J_1(A_0)} \right) \tag{1}$$

The splay elastic constant is obtained directly from the Frederiksz threshold voltage ($V_{th}$) and is given by $K_{11} = \varepsilon_0 \Delta \epsilon \left( \frac{V_{th}}{\pi} \right)^2$. At strong surface anchoring condition, the voltages above the threshold voltage ($V_{th}$) and the retardation ($\Delta \phi$) are given by the parametric equations: \[25, 26\]

$$\Delta \phi = 2\pi \frac{n_0 d}{\lambda} \left[ \frac{2}{\int_0^\infty \frac{1 + y \sin^2 \theta_m \sin^2 \psi}{1 - y \sin^2 \theta_m \sin^2 \psi} dy} - \frac{n_e}{n_c} \right] \cdot \left( \frac{1 + \sin^2 \theta_m \xi \sin \psi}{1 - \sin^2 \theta_m \xi \sin \psi} \right) d\psi \tag{2}$$

and

$$\frac{V}{V_{th}} = \frac{2}{\pi} \sqrt{1 + \gamma \sin^2 \phi_m} \times \left[ \frac{2}{\int_0^\infty \frac{1 + k \sin^2 \phi_m}{1 - \sin^2 \phi_m \sin^2 \psi} dy} \right]$$

$$\frac{\gamma}{\xi} - 1 \quad 1 \cdot \sin^2 \phi_m = \sin \phi_m \sin \psi$$

$$\begin{align*}
\text{where} & \quad d \text{ is the cell thickness, } \phi_m \text{ is the tilt angle at the middle of the cell and the other terms of the reduced quantities are } \gamma = \left( \epsilon_0 / \epsilon_\parallel \right) - 1, \quad k = (K_{33} / K_{11}) - 1,
\end{align*}$$

3. Results

3.1. Sample observation and thermal measurements

The liquid crystals used for the experiments are 8CB and 5CB. These compounds were obtained from Sigma-Aldrich and used without further purification. 8CB and 5CB exhibit the following phase transitions: Cr. 22°C SmA 32.5°C N 40°C I and Cr. 22.5°C N 35°C I. The BaTiO$_3$ nanoparticles were obtained by milling micron sized particles together with heptane and oleic acid (surfactant).\[29\] The details of the particle harvesting is discussed in \[30\]. The average size of the nanoparticles measured by transmission electron microscope is approximately 12 nm. It has been reported that the ferroelectricity is retained in these nanoparticles due to the compressive and tensile surface strain. The ferroelectric nanoparticles were suspended in liquid crystals and the solvent was evaporated. Two different concentrations of BaTiO$_3$ nanoparticles, namely, 0.2 and 0.4 wt% of both the samples, were prepared. Physical observations indicate that the dispersions are stable and homogeneous. Figure 1(a) shows that the suspension with 0.4 wt% of nanoparticle also appears like pure liquid crystal with no evidence of dispersion. We show the textures obtained under polarizing optical microscope for 5CB + 0.4 wt% BaTiO$_3$ nanocomposite in Figures 1(b) and (c), respectively. It is noticed that the director is uniformly oriented with no evidence of agglomeration of nanoparticles. The measurements were restricted to 0.4 wt% of nanoparticles as the agglomeration-free stable suspension (over a few months) was achieved approximately up to this concentration.

Figure 2 shows the differential scanning calorimetry (DSC) measurements of all the samples. It is observed that the nematic to isotropic transition temperature ($T_{NI}$) of 5CB liquid crystal decreases with increasing concentration of nanoparticles (Figure 2(a)). In particular, it decreases by about 2.5°C compared to the pristine sample although the enthalpy remains almost
unchanged ($\Delta H_{NI} \simeq 3 \text{ J/gm}$). The DSC data of 8CB samples are presented in Figure 2(b). It is observed that $T_{NI}$ decreases and the N to SmA transition temperature ($T_{NA}$) increases with increasing concentration of nanoparticles. The SmA to crystallisation temperature is also decreased compared to the pristine sample. For example, in suspension with 0.4 wt% of BaTiO$_3$ in 8CB, $T_{NI}$ is decreased by 2°C whereas $T_{NA}$ is increased by
1.5°C. Thus, the nematic temperature range is shortened and SmA temperature range is widened with increasing concentration of BaTiO$_3$ nanoparticles. We also measured the enthalpy of the respective phase transitions of 8CB and they are listed in Table 1. It is observed that the enthalpy ($\Delta H_{NI}$) of the NI transition decreases in both heating and cooling experiments compared to the pristine sample. On the other hand, the enthalpy ($\Delta H_{NA}$) of the N–SmA transition increases with the concentration of BaTiO$_3$ nanoparticles. For example, $\Delta H_{NA}$ of pristine sample is 0.41 J/gm whereas in suspension with 0.4 wt%, it is 0.66 J/gm and this is about 60% larger than the pristine sample.

### Table 1. Nematic and SmA temperature range and enthalpy of N–I and N–SmA transitions of 8CB and the colloidal suspensions.

<table>
<thead>
<tr>
<th></th>
<th>Cooling</th>
<th>Heating</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO$_3$ (wt%)</td>
<td>0</td>
<td>0.2</td>
</tr>
<tr>
<td>$\Delta H_{NI}$ (J/gm)</td>
<td>3.3</td>
<td>3.1</td>
</tr>
<tr>
<td>$\Delta H_{NA}$ (J/gm)</td>
<td>0.41</td>
<td>0.48</td>
</tr>
<tr>
<td>N range (°C)</td>
<td>6.9</td>
<td>5.5</td>
</tr>
<tr>
<td>SmA range (°C)</td>
<td>36.3</td>
<td>39.2</td>
</tr>
</tbody>
</table>

3.2. Birefringence and dielectric measurements

We measured birefringence ($\Delta n = n_e - n_o$) and dielectric anisotropy ($\Delta \varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$) of all the samples as a function of temperature. The variations of $\Delta n$ and $\Delta \varepsilon$ of 5CB as a function of relative temperature ($\tau = T_{NI}$) are shown in Figure 3. Both $\Delta n$ and $\Delta \varepsilon$ of 5CB remain almost unchanged compared to the pristine sample. The temperature variations of $\Delta n$ and $\Delta \varepsilon$ of 8CB are shown in Figure 4. It is observed that $\Delta n$ remains almost unaffected, and in addition, the enhancement of $T_{NA}$ is reflected in both the measurements in accordance with DSC measurements (Figure 2(b)). The small jump of $\Delta n$ at the N–SmA transition is about 0.007 and comparable to the value obtained by direct intensity measurement technique.[31] The perpendicular component of the dielectric constant $\varepsilon_{\perp}$ in the nematic phase of 8CB liquid crystal remains almost unchanged, whereas the parallel component ($\varepsilon_{\parallel}$) shows a small decreasing tendency with increased concentration of nanoparticles. For example, at $T - T_{NI} = -4°C$, in the suspension with 0.4 wt% nanoparticles, $\Delta \varepsilon$ is decreased by 10%.

3.3. Elastic constant measurements

Figures 5 and 6 show the temperature variation of splay ($K_{11}$) and bend ($K_{33}$) elastic constants of both the samples and various suspensions. In the pristine sample, both $K_{11}$ and $K_{33}$ are comparable to the previously reported values.[32, 33] When they are compared with relative temperature, it is observed that there is no significant change in $K_{11}$ (Figures 5(a) and 6(a)), whereas $K_{33}$ decreases considerably (Figures 5(b) and 6(b)). For example, in both samples, at 0.4 wt% of nanoparticles, it decreases almost 20% compared to the respective pristine samples.

3.4. Rotational viscosity measurements

Rotational viscosity was measured by using a phase-decay-time measurement technique.[34] First ac voltage-dependent (frequency 1 KHz) transmitted intensity in a planar aligned cell was measured. A small voltage ($V_b$) corresponding to first minima or maxima of the transmitted intensity was applied, and at time $t = 0$, the voltage $V_b$ was removed and the relaxation transmission intensity change was measured. The time-dependent transmitted intensity at a particular temperature is given by $I = I_0 \sin^2[(\Delta \delta(t))/2]$, where $I_0$ is the maximum intensity and $\Delta \delta(t)$ is the
total phase difference. The optical phase difference \( \delta(t) = \delta_0 \exp(-2t/\tau_0) \), where \( \delta_0 \) is the total phase difference under bias voltage \( V_b \). The slope of the plot \( \ln(\delta_0/\delta(t)) \) with time \( t \) gives the relaxation time \( \tau_0 \).

Rotational viscosity is given by \( \gamma_1 = \pi^2 K_{11} \tau_0 / d^2 \), where \( d \) is the cell thickness. The variation of \( \gamma_1 \) of both 5CB and 8CB liquid crystals at various concentrations of nanoparticles is shown in Figure 7. Rotational viscosity increases in all the samples with decreasing temperature as expected. More importantly, at a relative temperature, it decreases with increasing concentration of nanoparticles. For example, in 8CB at \( T - T_{NI} = -2^\circ \text{C} \), \( \gamma_1 \) decreases from 0.04 to 0.03 Pa s. This is about 25% reduction compared to the pristine sample. It may be mentioned that \( \gamma_1 \) is a derived quantity and depends on \( K_{11} \).

The reduction in \( \gamma_1 \) is entirely due to the decrease of the relaxation time as \( K_{11} \) remains almost unchanged.

4. Discussion

There are several studies on the N–I and N–SmA phase transitions in nanoparticle-dispersed liquid crystals.[35–37] It has been found that in aerosil-dispersed liquid crystals, both \( T_{NI} \) and \( T_{NA} \) decrease.

[37, 38] In case of ferroelectric nanoparticles, such as SnO_{2}P_{2}Se_{6}, it is reported that \( T_{NI} \) can increase or decrease.[39] Gupta et al. showed that \( T_{NI} \) decreases in 4-n-octyloxy-4’-cyanobiphenyl liquid crystal doped with BaTiO_{3} nanoparticles.[40] In colloidal systems with BaTiO_{3} nanoparticles, in a negative dielectric anisotropy nematic liquid crystal mixture, \( T_{NI} \) is reported to get enhanced.[41] From the temperature-dependent birefringence measurements, Mertelj et al. reported that \( T_{NI} \) decreases whereas \( T_{NA} \) increases with concentration of BaTiO_{3} in 8CB liquid crystal.[31] The decrease of \( T_{NI} \) was attributed to the contribution of the free oleic acid molecules. The increase of \( T_{NA} \) was argued due to the increase of de Gennes coupling coefficient \( C \) in the relation \( \delta S = \chi(T)C|\psi|^2 \), where \( \delta S \) is the increase in the nematic order parameter, \( \psi \) is the SmA order parameter and \( \chi(T) \) is the response function.[31] This could be a pointer to the fact that the oleic acid molecules act like a mesogenic dopant in 8CB liquid crystal. The typical length of a fully stretched oleic acid molecule is about 19.7 Å, which is almost comparable to the typical length of a 8CB molecule (22.1 Å). However, in the low melting form of oleic acid, a cis-double bond introduces a pronounced bend in the alkyl chain.[42] Thus, the
oleic acid molecules may act as a dopant similar to that of a bent-shaped molecule. Another interesting aspect is the significant change in the enthalpy values of the respective transitions. The decrease of enthalpy corresponding to the N–I transition (see Table 1) suggests that the first-order N–I transition is weakened due to inclusions. On the other hand, the enthalpy of the N–SmA transition is increased suggesting that this weakly first-order transition is becoming relatively stronger with the inclusions. Thus, the increase of $T_{NA}$ is consistent with enhanced enthalpy of the N–SmA transition.

There are several reports on the phase transitions and physical properties of the binary mixture of rod-like and bent-core liquid crystals. Here, we cite a particular example that reports on the effect of doping of bent-core molecules in rod-like nematic system. Pratibha et al. reported that in binary mixtures of rod-like and bent-core liquid crystals, $T_{NI}$ decreases whereas $T_{NA}$ increases with the concentration of bent-core molecules.[43] In the same system, we reported that $K_{11}$ remains almost constant whereas $K_{33}$ decreases with increasing concentration of bent-core molecules.[23] The shift of N–I and N–SmA phase transition temperatures and the variation of the physical properties in our present system as discussed are somewhat similar to that reported in [23, 43]. In the mean field theory, $K_{ij} \propto S^2 \propto \Delta n^2$, $\Delta n$ and $S$ being the birefringence and orientational order parameter, respectively. In the present systems, no significant change in $\Delta n(\times S)$ is observed (Figures 3(a) and 4(a)) except the order parameter increases more steeply with decreasing temperature in 8CB. Hence, elastic constants are expected to remain unaffected and it is seen only in case of $K_{11}$ (Figures 5(a) and 6(a)). However, it is known that $K_{33}$ may decrease in the binary system of rod and bent-core molecules due to the shape of the bent-core molecules keeping the orientational order the same.[23] This is due to the strong coupling of bent shape with the bend distortion.

The small concentration of BaTiO$_3$ nanoparticles does not significantly alter the dielectric constants and hence the anisotropy, except a tendency to decrease the parallel component of the dielectric constant ($\epsilon_1$). This suggests that either the ferroelectricity of the particles is lost or the effective polarisation of the nanoparticles is screened by the ionic impurities. The ion screening effect in similar systems has been
5. Conclusion

To summarise, we have performed DSC, birefringence, dielectric and viscoelastic measurements of colloidal systems of BaTiO$_3$ nanoparticles and two liquid crystals (5CB and 8CB). We found that apart from the nanoparticles, the free oleic acid molecules also significantly affect the phase transition and physical properties. The DSC data suggest that the temperature range of nematic is decreased whereas the temperature range of SmA is increased with increasing concentration of nanoparticles. In addition, the N–I transitions become relatively weaker and the N–SmA transitions become relatively stronger with concentration of BaTiO$_3$ nanoparticles. The birefringence, dielectric anisotropy and splay elastic constant remains almost unchanged. We provided a possible explanation on the reduction of bend elastic constant based on the effective shape of the free oleic acid molecules.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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References


